Occurrence and Fate of Alternative Flame Retardants in the Environment

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Chapter 5. Discussion and conclusions

International comparability

The increased use and production of PFRs after the ban and phase out of specific BFRs and the observed elevated levels of PFRs in the indoor (PUR foam, electronics, house and car dust) and outdoor environment (sediment, sludge and biota) has triggered many researchers to study this group of FRs (Fries et al., 2001; Meyer and Bester, 2004; Marklund et al., 2005; Reemstra et al., 2008; Stapleton et al., 2009; Mihajlovic et al., 2011; Van der Veen and De Boer, 2012; BCC research, 2013; Brandsma et al., 2014). This was one of the reasons of organizing an interlaboratory study on the analysis of PFRs. During the organization for this study many laboratories responded that they had not a validated method available yet. The outcome of the first interlaboratory study (*Chapter 2.1*) showed that indeed further improvement is needed on the analysis of PFRs in the indoor and outdoor environment. Therefore, it is highly recommended to organize a second interlaboratory study to improve the comparability and reliability of the data published by international laboratories, and assist laboratories to improve their methods of analysis of these FRs. As with other complex analytical methods, one could think of an approach based on stepwise-designed learning exercises, starting from clean extracts and working towards the analysis of real world matrices, giving dedicated advice after each step. Important matrices will be dust, indoor air (PUFs), sediment and water. For PFR metabolites blood and urine may be important matrices.

Method development: PFRs in Biota

It was found that the removal of lipids was the most critical factor in the analysis of PFRs in biota. Finally, a clean-up method based on SPE column with a NH_2 stationary phase was selected as the optimum method for lipid separation after testing various cleanup methods. The selection of SPE-NH_2 column was made based on the following results. Acid treatment, which is a commonly used cleanup method for PBDEs, could not be used due to the degradation of PFRs. Gel permeation chromatography (GPC), with dichloromethane (DCM) as mobile phase, was not successful due the overlap of PFRs with the lipids fraction. Separation of the PFRs from lipids could be performed with Al_2O_3 (8% H_20 w/w) using a mixture of 30% (w/w) DCM in pentane where the lipids eluted first, followed by the PFRs using 100 % diethyl ether. However, this method showed poor recoveries for TPHP and TBOEP. A fractionation method with silica gel (1.5% (w/w) H_2O) showed that in the first fraction the lipids were found, in the second fraction three cyclic PFRs (TPHP, TMPP and EHDP) and in a third fraction the other PFRs. However, the third fraction, with most of the PFRs, still contained 6 - 20% matrix constituents, depending on the sample. Therefore, an additional cleanup step was needed.

Further clean-up of the third silica gel fraction with SPE columns were tested but still contained some matrix (Table 1). SPE columns tested were HybridSPE^{TM}-PPT (SUPELCO, Bellefonte, USA), Oasis® HLB (Waters, Milford, USA) and Discovery® DSC-NH_2 (SUPELCO, Bellefonte, USA). The different condition for each SPE method is given in Table 1.

Table 1. Conditions used for the three SPE methods.

	SPE-PPT	SPE-HLB	SPE-NH_2
Washing	10 mL DCM	10 mL DCM	10 mL DCM
Conditioning	6 mL hexane	6 mL hexane	6 mL hexane
Introduction of sample	in 500 µL hexane	in 500 µL hexane	in 500 µL hexane
Rinsing volume	2 X 500 µL hexane	2 X 500 µL hexane	2 X 500 µL hexane
Washing solvent (Fr 1)	5 mL hexane + 2mL 30% DCM in hexane	5 mL Hexane	3 mL Hexane
Elution of PFRs (Fr 2)	15 mL acetone	10 mL DCM	4 mL 20% DCM in hexane + 15 ml DCM

SPE-HLB had no effect on the matrix removal, while PFRs eluted in the matrix fraction as soon as traces of DCM were present from the extract. SPE-PPT and SPE-NH_2 showed the best results to remove the matrix. The limitation of the SPE-PPT column was the strong retention of the cyclic PFRs, which resulted in low recoveries of TMPP and TPHP, 10 and 24%, respectively. Because the cyclic PFRs were separated from the aliphatic PFRs with silica gel, SPE-PPT is a suitable method if used in combination with silica gel.

Another approach is to simplify the method by using only SPE-NH_2 instead of a combination of silica with SPE-NH_2. The simplification of the method has one other big advantage, which is the reduction of background levels of PFRs from the materials used; ng level-blank values were observed for TIBP, TNBP and TBOEP when silica was used. Silica gel cleanup involves more glassware and evaporation steps in which background contamination can be introduced. The results of the silica/SPE-NH_2 cleanup in comparison with a SPE-NH_2 cleanup alone are shown in Table 2. For all matrices the cleanup with SPE-NH_2/silica is 10% more effective than without silica. However, the blank values for the SPE-NH_2 cleanup without silica are 5-10-fold lower for TIBP, TNBP and TBOEP. Therefore, SPE-NH_2 alone was chosen as the optimum method and was further validated in *Chapter 4.3*.

Table 2. The results of the silica gel fractionation of fish oil, bird eggs and sole, followed by a cleanup of the third silica fraction by three different SPE methods. Also shown is a cleanup with SPE-NH2 only.

	Fish oil				**Bird egg**				**Sole**			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
Lipids (gram)	0.25	0.23	0.26	0.25	0.16	0.19	0.24	0.24	0.14	0.15	0.25	0.26
Silica F1	81%	78%	79%		76%	80%	86%		43%	51%	70%	
Silica F2	4%	4%	4%		1%	2%	1%		9%	8%	5%	
Silica F3	13%	14%	13%		8%	7%	6%		20%	19%	21%	
Retains on the silica	1%	4%	4%		14%	12%	6%		28%	22%	4%	
	SPE-PPT	SPE-HLB	SPE-NH2	SPE-NH2*	SPE-PPT	SPE-HLB	SPE-NH2	SPE-NH2*	SPE-PPT	SPE-HLB	SPE-NH2	SPE-NH2*
SPE F1	0%	1%	0%	69%	0%	1%	0%	70%	0%	0%	1%	58%
SPE F2	5%	12%	7%	17%	6%	6%	6%	18%	10%	18%	7%	20%
Retains on the SPE	8%	2%	6%	14%	2%	0%	0%	12%	10%	0%	13%	22%

*Without silica cleanup

Because only non-destructive cleanup methods can be used for the analysis of PFRs in biota, further improvement of the cleanup method is difficult. One of the conclusions from *Chapter 4.3* was that PFRs, in contrast to BFRs, are not correlated to the lipid content of samples. During the method development we mainly focused on the removal of lipids. Further investigations should therefore

focus on the amount of tissue instead of the lipid content. Lower fat intakes of lean fish would therefore still result in detectable levels with less matrix interferences during cleanup. Another option to improve the analysis of PFRs in biota is to further optimize the detection limit of the analytical equipment (mass spectrometer, LC column). For example, Kim et al. (2011) used a dilution step (10 times) before cleanup, which was possible due to the optimized analytical method, which was up to 10-fold more sensitive by using ultra high performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS).

Transfer of FRs from product to dust

PBDPP and BPA-BDPP were detected in different consumer product (*Chapter 3.1*). The same FRs were also detected in house dust samples, with the highest levels in dust taken from the electronic equipment (*Chapter 4.2*). The results of the leaching experiment show that PBDPP and BPA-BDPP do not leach from the polymer material into a buffered solution (*Chapter 3.2)*. Within the ENFIRO project also test chamber experiments were performed, according to the method of Kajiwara et al., (2010) with some modifications, to measure the emission of PBDPP and BPA-BDPP from polymer materials to the air. Both PBDPP and BPA-BDPP were not detected in the air (<0.02 , <0.005 pg/cm^2/day, respectively) after 60 days by room temperature or 40 °C. Only at a higher temperature of (80 °C) low levels of PBDPP (0.7 and 1.1 pg/cm^2/day) were detected after 7 days. Another study by Kemmlein et al. (2003) observed an emission of 20ng/m^3 of BPA-BDPP and 13 ng/m^3 of PBDPP from a personal computer to air in a test chamber study. The results of the leaching and test chamber studies could not explain the elevated levels (µg/g levels) observed in the house dusts. Recently Tsunemi et al., (2014) found evidence that BDE209 and BPA-BDPP diffuse from the polymer to glass beats by direct contact. Also Rauert et al., (2014) hypothesize that beside volatilization and abrasion of fine particles to dust, direct contact of dust with the polymer material may play an important role during the migration of FR to dust. Therefore, more research is needed to better understand the mechanism behind the process of migration of FRs from products into dust. Especially, the direct contact of dust with polymer material should be further investigated. This information could help to predict the exposure of humans to FR from polymer materials and products. The representativeness of the leaching tests is another subject of further study.

Collaboration and future perspectives

Within the ENFIRO project researchers of industry worked together with universities and research organizations to search for viable alternative FRs for specific BFRs that are not toxic, persistent, and bioaccumulative, are not expensive and easy to incorporated into the polymer. Unfortunately, this approach is not often seen. There are still many different commercial FR mixture on the market as alternatives for specific BFRs that show structural similarities with banned substances, because their

structure were only slightly changed, e.g. by replacing a chlorine atom by a bromine one or by extending the carbon chain. These novel FRs have already been detected in the indoor and outdoor environment which indicated that humans are exposed to different FR mixtures of which toxicity information is limited (Covaci et al., 2011; Van der Veen and De Boer, 2012). Also in this thesis we describe the finding of two alternative FRs mixtures (BPA-BDPP and PBDPP) in house and car dust.

The use of restricted FRs may not only have effect on the environment and human health, but may also have influence on the waste and the recycling phase of polymers. For example, the European Union Directive 2011/65/EU puts restrictions on hazardous substances (RoHS) in products. PBDEs in electrical and electronic equipment are limited to <0.1% of the material. Less information is available on PFRs in plastics and polymer materials. However, recycling of polymers containing FRs may lead to recycled polymers containing different mixtures of FRs (Leslie et al., 2014). FRs may also end up in products where they are not needed, like children's toys. (Chen et al., 2009; Ionas et al., 2014). This indicates that some products cannot be recycled due the use of restricted FRs in the past. That is why it is so important that before an FR is used in a polymer application, it is thoroughly tested. It should also be checked if the FR is really unavoidable in the application. This is essential to ensure that in the future the use of the FRs has no negative effect on human health and the environment and will also not interfere with the recycling processes. The ENFIRO project has delivered a very valuable approach that can play an important role in these decision making processes.

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